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What Should Be Done to Mitigate Groundwater Contamination?

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Groundwater contamination is a serious problem that is growing in the United States, but its true extent is not known and it is difficult to determine because of the complexities of contaminants, their transformation, and fate in groundwater systems. It is also difficult to predict their movement in groundwater. Since we know that the problem is serious and that our needs for groundwater will grow, the mitigation of groundwater contamination, despite the high cost, is necessary. Furthermore, it is very difficult to predict effects on human health because they have not been defined for many of the chemicals. Antagonism and synergistic effects of interacting chemicals have not been determined because they are complicated by many factors, for example, volatile organic compounds. The effects of leachates in groundwaters entering streams on the riverine environment and aquatic life have not been determined.

Successful mitigation requires that we determine which microbial and chemical contaminants are the most serious threats to human health, develop the technology to biologically, chemically, and physically transform hazardous waste into nonhazardous materials; develop the technology to properly contain hazardous materials and to remediate contamination, and determine the effects of those hazardous materials on soils and water microorganisms and macroorganisms. Our challenge is how can we immobilize or destroy groundwater contaminants so that they will not enter groundwater, or if they enter groundwater, are confined and destroyed.

Introduction

Groundwater contamination is present in every state of the union; however, its true extent is not well known because of lack of detailed mapping in most states. Estimates by the U.S. Environmental Protection Agency (EPA) are that up to 1% of the known usable aquifers near the land surface may be contaminated. Lehr (*1*) estimates that this may be as much as 2%.

There are several reasons why we do not know the extent of groundwater contaminations. One is that the movement of groundwater is very slow and complex; it may move rapidly if it is pumped or under a hydrolic head. Contaminants may or may not move with groundwater, because many factors effect their movement. For example, the specific gravity or density, which is the specific gravity as it relates to water, varies greatly for different chemicals. Therefore a contaminant may float, it may sink to the bottom of the aquifer onto the aquitard, and in some cases it may move in an opposite direction to the flow of water in the aquifer (*2*). The movement may be complex because aquitards often have fissures in them, and the movement through a fissure is much faster than movement in the aquifer. Furthermore, the aquitard, particularly in limestone, may have various lacunae in it, where the contaminant is held, and may continue to contaminate the aquifer for a long time. Several years ago, we thought that aquifers were separate and that the aquitard was impervious. We now know that an unconfined aquifer may contaminate a confined aquifer. Understanding the movements of contaminants is an active field of research.

Types of Aquifer Contaminants

The contaminants may be divided into two general groups—organisms and chemicals. The organisms that cause illnesses are mainly bacteria and viruses; although protozoans, a few worms, and fungi have been found to cause illnesses from the drinking of groundwater. We do not know all of the symptoms or causes of illnesses from contaminants. The most commonly reported contaminants are organics, microorganisms, and nitrates. There are certainly many thousands of chemicals that are potential contaminants of groundwater. However, at the present time, the number of diseases or illnesses caused by chemicals are very few compared to those caused by organisms. Craun (*2*) estimates that there were 8558 illnesses caused by microbial contamination from the use of untreated well water. Chemical contamination was responsible for only 157 of the illnesses (*2*).

Although we have an estimate of the number of chemicals that may be placed on the ground, we do not know very much about what happens to many of these chemicals when they pass through the soil profile. For exam-

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ple, evidence for biotransformation of trace halogenated organic compounds in the subsurface was observed in a groundwater recharge project at Palo Alto (California baylands) where reclaimed municipal waste water was injected into a confined aquifer (*3*). Within 50 days after stopping injection, the concentrations of chloroform and other trihalomethanes at a near-by observation well were found to decrease significantly. A much slower decline occurred in the concentration of chlorinated ethanes and ethenes. Several halogenated alleophatic compounds were apparently degraded during soil perculation in the anoxic subsurface between waste water infiltration basins in Phoenix, AZ (*3*).

In the Netherlands, it was found that no halogens were detected after perculation through dune sand, despite relatively high haloform concentrations (20–100 mg/L) in the influent water, suggesting a removal by biotransformation under anoxic conditions. Degradation can be enhanced for gasoline components when oxygen, nitrogen, phosphorus, and other trace elements are added to the aquifer. Evidence for 1,4-dichlorobenzene degradation was found under aerobic conditions within an apparent half-life of 8 days during infiltration from the Glatt River. Subsurface biological activity caused the aquifer to go anoxic in the summer months; during this period, 1,4-dichlorobenzene was observed to persist. Also, in the strictly anaerobic segment of a plume 1,2,4-trichlorobenzine and 1,4-dichlorobenzene were equally persistent, but they were down-graded in the less anaerobic region; the former appeared to be degraded more rapidly than the latter. More than 80% conversion of nine of the ten halobenzoates and five of seven chlorophenols, and two of the two phenoxyacetic acid herbicides were transformed in methanogenic aquifer samples and were not observed in sulfate-reducing aquifer samples (*4*). Degradation of a number of alkylbenzenes, in methanogenic aquifer material after long lag periods has been reported. Benzene, ethyl benzene, and *O*-xylene degraded in up to 40 weeks, and 6 weeks of acclimation time was needed for toluene degradation. Halogenated aliphatics such as trichloroethylene were transformed with the lag period of a few weeks (*3*).

Subsurface microorganisms that were isolated from aquifer material and groundwater collected at an abandoned creosoting site in Texas, could utilize anthrazene, dibenzofurans, fluorine, and naphthalene as a sole source of energy. Hexachloroethane has also been found to disappear rapidly when introduced into an unconfined sand aquifer with the half-life of 40 days (*3*).

Microbial activity is influenced by environmental factors such as pH, temperature, salinity, soil moisture, and different kinds of nutrients such as nitrogen, phosphorus, calcium, and magnesium, as well as by trace elements such as iron, manganese, and cobalt. The redox potential in the environment also has a great influence on the kinds of compounds that can be biotransformed. Some compounds can be degraded only in aerobic conditions; others degrade only in the absence of oxygen. Other compounds degrade under several different redox conditions. The concentration of the pollutant also effects the ability of microorganisms to carry out biotransformation. At very low concentrations there may be insufficient energy available to support biomass growth. If bacteria are provided with the primary substrate at sufficiently high concentrations to support bacterial growth, then they may be capable of degrading a trace contaminant while using it as a secondary substrate.

Acclimation time of organisms before they can transform different chemicals is variable and often hard to predict. Thus, it is evident that there are many factors that effect the biodegradation of chemicals. Much more information is needed to understand this biotransformation under various subsurface environments before the most effective use of this type of transformation can be made.

Gibson and Suflita (*5*), found that under anaerobic conditions some compounds such as haloaromatic chemicals are degraded in methanogenic incubations by reductive dehalogenation reactions. Complete dehalogenation was required before the aromatic ring could be mineralized, and no dehalogenation occurred when sulfate-reducing conditions existed. In contrast, the degradation of cresol isomeres was favored under sulfate-reducing instead of methanogenic conditions (*6*). Thus, it is evident that under anaerobic conditions various chemicals can be degraded and the types of chemicals degraded differ under methanogenesis and sulfate-reducing conditions.

The recent discoveries at the Savannah River Plant indicate that there are more than 2000 physiologically different bacteria at a depth of 700 ft. This suggests the potential of many unusual metabolic pathways that may be found to be important in the biodegradation of various types of chemicals.

Other types of transformation may occur by chemical and physical processes such as precipitation, chelation, and ionic exchanges of various types between the medium and the contaminant as it passes through the soil profile. New methods of extracting by high heat, by electrical reactors, and, perhaps by microwaves and by use of infrared are other ways of destroying hazardous materials. Capsulation in molten glass or ceramics is a promising method for radioactive contaminants and very toxic wastes.

In considering the effects of contaminated groundwater, one is most concerned with the effects on human health, and secondarily but importantly, the effects on the environment. Our knowledge of the effects on human health are not very exact; therefore, precise answers are difficult to obtain. The effects of antagonism and synergism of chemicals in many contaminants have not been determined.

Two of the greatest limitations of epidemiological investigations are the lack of ability to precisely estimate human exposure to a chemical or mixtures of chemicals and the influence of potentially confounding variables. For example, the epidemiological studies concerning chlorination of water and cancer risk were of an ecological nature (*6*). These studies compared cancer rates in communities with chlorinated surface waters versus communities having drinking water that was derived from groundwater. For the most part, these studies did not include the historical levels of trihalomethanes or other carcinogens. Nor did they have evidence of the water consumption patterns; occupational exposures to carcinogens or early childhood exposures to harmful agents or medications; dietary consumptions of natural carcinogens; or the level of dietary promoters such as fat (*7*). These studies usually assume that these factors are similar among the comparison communities, but the assumption is usually not verified, let alone reconstructed in the historical profiles reaching back over three to four decades. More recently, mathematical models for estimating past chloroform levels in drinking water have been made, but this is only an initial step because of the long latency between initiation of tumorigenesis and the clinical manifestation of cancer. Epidemiological studies are always going to be difficult to sufficiently characterize exposure for use in quantitative risk assessment. Also the frequent moving of the population of citizens from one area to another complicates any epidemiological studies (*7*).

Volatile organic compounds can also complicate such epidemiological studies. It has been shown that a significant percentage of volatile organic chemicals in shower water becomes stripped from the water; these chemicals are available for inhalation. Additionally organic carcinogens in potable water possess some degree of lipophilicity. This supports the hypothesis that bathing in such waters may result in dermal absorption. Brown et al. (*8*) argue that dermal absorption of organic contaminants from drinking water may result in several-fold greater exposures over the absorption from water consumption (*6*). Most of our studies on carcinogenity have been based on animal studies, mainly on mice and rats. These two animals have been found to vary in their susceptibility to various chemicals forming cancer. Furthermore, because of the differences in enterohepatic circulation, the ability to predict the effects from rat or mouse experiments to humans is very difficult. Furthermore, it has been found that the administered dose may be different than the dose received to the critical tissue. Additionally, literature has reported that host factors such as age, sex, diet, genetic make-up, and predisposing disease conditions may effect susceptibility to chemically induced cancer. It should be pointed out that the problem of trying to verify low-dose cancer risk predictions for example, in 10^{-5} or 10^{-6} concentration of chemicals is very difficult and expensive. Furthermore, validating that a risk of 10^{-6} concentration may be off by one or two orders of magnitude in either direction is probably not verifiable with current epidemiological methodologies, or so-called megamouse studies (*6*).

These various examples emphasize the many difficulties in calculating risks to humans from a given carcinogen. The necessity is clear; much more research for the development of more exact methods for epidemiological studies for estimating human risk to a given chemical must be done.

Although the ability to estimate effects on human health of hazardous chemicals needs a great deal more research, we know much less about the effects of small amounts of various types of chemicals on the environment. For example, we know that many plants have a microflora and fauna that are very important in the cycling of nutrients for a particular plant species. If this microflora is damaged, the productivity or yield of the plant crop will be effected. For these reasons, any chemical in the soil that hinders such activity may have a significant effect on the production of a given crop or various crops. Furthermore, leachates from groundwater contaminants passing through the ground may greatly alter the composition of the fauna and flora of the soil; as a result alter the cycling of nutrients in the biosphere, e.g., nitrogen cycling. Furthermore, if these chemicals are bioconcentrated within the plant crops that are eaten by human beings, they may pose a real threat to human health. Such studies are very limited, and, as yet, we do not have a picture of the effects of groundwater contamination on the environment and indirectly human health.

Another type of environmental effect of leachates, or contaminants in groundwater, is the effect upon riverine species. It is well known that approximately one-third the fresh-water flow of all rivers is groundwater, and during droughts all of the flow of a continuous flowing stream is groundwater. As a result, the organisms are effected by the characteristics of the groundwater. Thus it is apparent that very small amounts of toxic substances may alter the aquatic communities in streams and thus alter the ability of a stream to assimilate wastes, which would greatly effect the quality of water for human use.

Recent surface water studies have clearly shown that algae may bioaccumulate many thousand times the ambient concentration of hazardous chemicals in water (*9*). These algae are often the primary food of invertebrates and, hence, of fish, and thus the contaminants that may enter a stream from groundwater can become a threat to human health.

What Does the Future Hold in Store?

As we look into the future, it is very evident that the populations of the world are going to become more and more dependent on groundwater. The question is, "How can we prevent or if not prevent, greatly reduce the trend of toxics to spread in groundwater?" The best way to prevent contamination is at the source, but we will never prevent all contamination because all organisms, including man, produce contaminants and these eventually may enter the groundwater. The principle sources of groundwater contamination are very different in various parts of the country, and the effects on humans vary, depending on the transformation of these chemicals as they pass through the soil profile. We need to learn about these transformations and their interaction with other chemicals that may be associated with them before we can make more exact predictions as to the seriousness of effects on human health.

Since it will always be impossible to eliminate wastes and all chances of groundwater contamination, and since it will take time to carry out the necessary research, the question is, "What can we do in the immediate future to most effectively mitigate groundwater contamination?" Besides the control at the sources, one can control the wellhead areas and prevent the use of the area that is in the draw-down area of a well for purposes that might produce groundwater contamination. The careful control of the use of recharge areas of aquifers is also necessary. Another method for reducing contamination is the classification of aquifers as to quality and quantity and restricting their use to conform with these parameters. Restrictions on overpumping are important because this practice often produces contamination, causing the water from contaminated aquifers to flow into an uncontaminated aquifer. This can be controlled by carefully monitoring the waterhead in the aquifer.

Another method of reducing the threat of contamination is by remediation. There are several approaches to this type of control. One is the fixing of chemicals within a landfill or other contaminated areas by various methods to prevent the leachate from leaving the landfill. Second is the volatilization by the injection of air into a lagoon or dump to drive off the volatile materials that are captured and destroyed. Such procedures can also be used to detoxify an aquifer that has volatile materials in it. This is done by placing the source of air at the base of the aquifer.

Biotransformation, which has been discussed above, is a means of reducing the toxicity of contaminants that are in aquifers or that have the potential of entering aquifers. This is a very important area of research and offers great promise for the future. In a similar way, we need to learn much more about chemical interactions that precipitate or chelate or bring about various types of ionic exchange that either transform a chemical that is toxic or bind it so that it is relatively harmless.

Another approach would be to use new methods of constructing basins. These would contain concentrated toxicants that could not otherwise be removed.

From the previously discussed material, it is very evident that the mitigation of toxic or hazardous wastes is one of the most costly problems facing society. Our ignorance of what to do is colossal. We must at once harness the best brains in the country to do the following: *a*) determine which chemicals and/or organisms are most harmful to human health and the environment, and put our first efforts into controlling them. This means more exact knowledge as to the actual dose which produces harm, be it to humans or to organisms in the environment. For human populations, this determination can only be accomplished by greatly improving epidemiological methods and more rapid means of determining the deleterious effects of hazardous substance that may have severe chronic effects. *b*) We must support research that will determine how hazardous materials can be transformed to nonhazardous chemicals by biological, chemical, and physical processes. *c*) We must develop means to confine or prevent the spread of hazardous materials and, where possible, remediate them by biological, chemical, and physical processes. *d*) It is important that we better understand the effects of hazardous materials on the microorganisms and macroorganisms of the environment that play such an important role in the soil and in the water. It is these organisms that make possible the cycling of nutrients and the maintenance of a natural environment which is so important to human health.

These requirements mean the elimination or a great reduction of the source of toxic or hazardous materials in effluents—be they from industry, municipal plants, or nonpoint sources such as farms and septic tanks, small businesses, or homes. It means the reduction of potential hazardous materials entering the aquifer by the protection of wellheads and recharge areas: by the inspection of septic tanks and underground storage tanks and pipelines; and by continually monitoring them. It means developing a meaningful basis of classification of aquifers based on their natural characteristics, so that we can better understand what chemicals might be interactive or produce little change if they occurred in these aquifers and which ones would cause a severe alteration of the natural characteristics of the aquifer. It means more precise understanding of the ultimate effects of mixtures of contaminants on human health.

To implement these objectives, we must train and, if need be, retrain decision-makers and technical people to implement the most effective ways of reducing wastes, and manage these wastes so as to mitigate their hazardous effects. Through research we must produce more accurate epidemiological methods and a more exact knowledge of potential effects on human health of mixtures of chemicals in the ground.

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